

Removal of Malachite Green Dye from Water Using Orange Peel as an Adsorbent

Thesis Submitted

by

VIJAYA LAXMI (212CH1076)

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Dr. SUSMITA MISHRA



DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008

Certificate



**Department of Chemical Engineering
National Institute of Technology
Rourkela -769008, India**

This is to certify that, Vijaya Laxmi, a student of M.Tech, 4th Semester, Chemical Engineering Department, NIT Rourkela bearing Roll No. 212CH1076 has completed his final project on the topic “*Removal of Malachite Green Dye from Water Using Orange Peel as an Adsorbent*” under my guidance successfully. She has shown an authentic work with valid results and submitted a complete thesis of the work as required according to the curriculum in partial fulfillment for the award of M. Tech. degree.

Date:

.....
**Dr. (Mrs.) S. Mishra,
Associate Professor,
Chemical Engineering Department,
NIT Rourkela.**

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Date-

**VIJAYA LAXMI
Roll no. 212CH1076**

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ABSTRACT

The objective of this project work is to study the adsorption of Malachite Green dye using orange peel adsorbent. Cheap and eco-friendly adsorbent has been used for removal of malachite green dye from aqueous solution. Liquid phase batch operations were carried out to observe the effect of various experimental parameters such as contact time, temperature, pH, initial concentration of malachite green, adsorbate dose and the optimum conditions for these parameters were evaluated. Various characteristics of the orange peel sample were also examined. Study of adsorption kinetics and adsorption isotherms was carried out and best fitting models for rate kinetics and isotherms were suggested. The kinetic experimental data was analyzed using two kinetic equation-pseudo first order equation and pseudo second order equation. It was observed that it followed the pseudo first order equation. The Langmuir and Freundlich isotherms were used to fit the equilibrium data and the results showed that the Langmuir isotherm seemed to agree better than the Freundlich isotherm. The Gibbs energy was calculated which showed that it is an exothermic reaction. The results indicated that orange peel can be used as a good low cost alternative for treatment of effluents containing malachite green in water.

KEYWORDS: adsorption, dye, orange peel, rate kinetics, isotherm

Chapter 1

Introduction

1. INTRODUCTION

1.1 Water Pollution

The presence or introduction of unwanted materials in the environment which have harmful or poisonous effects is called Pollution. It is the introduction of contaminants in the surroundings which have adverse effects. There are numerous forms of pollution which exist these days like air pollution, water pollution, and noise pollution. The different constituents of pollution which are called pollutants may be either contaminants which are already in nature or those which have been come onto existence due to human activities. Pollutions might be present in the form of any organic or inorganic materials or sometimes some kind of energy like sound, light etc.

Water pollution has become one of the most dangerous threats to environmental in today's world. It is the impurification of water resources-rivers, oceans, groundwater etc. because human beings and their activities. There are various ways of polluting water, most important being the discharge of industrial waste water through spillage from into water bodies. The sewage discharge from homes is not treated before being discharged to environment which is also a main cause of pollution. Other causes include chemicals which are flowing on the surface due to various activities and fertilizers and pesticides release from the agricultural activities.

Thus it can be concluded that any kind of change in properties of water which may be physical, chemical or biological and which have harmful consequences is water pollution. The effects of water pollution are not limited to human beings, but it is fatal for the entire ecosystem. Water comes from many sources like ground water, surface water, that is why its cause of pollution also are various depending on the sources. Chemical, textiles, tannery industries etc. cause high rate of pollution. The waste water containing heavy metals, chemicals, dyes, oils and many other harmful materials are discharged by the industries into the water bodies without proper treatment, thus leading to contamination of water bodies. The dreadful effect of water pollution can be easily be guessed by the fact that today, polluted drinking water has become a major concern for mankind. There are more than 300 million cases of water-borne diseases every year, which leads to the death of approximately 8 to 12 million people. In developing countries like India, more than 60 percent of harmful wastes are thrown into water bodies where they

contaminate the water available for use. Approximately, 600 persons in India die of water pollution related illness every day in India. Due to these catastrophic effects of water pollution, it has become very important to find out different ways for treatment of waste water owing to the importance of pure water for the existence of mankind.

1.2 Dyes

A dye is a coloured substance which has a tendency to get attached to the substance on which it is being applied. In most of the cases, the application of dye is in the form of aqueous solutions. For better performance of dye on the fiber, some external substances called mordent are used. Both dyes and pigments appear to be colored because they absorb some wavelengths of light more than others. There are various reasons because of which dye possess; the most basic reason being that it absorb light in the visible spectrum (400–700 nm). Also because they contain colour-bearing groups called chromophores. Also, the structure of dyes possess double and single bonds alternatively the last reason being that dyes shows resonance property which stabilizes organic compounds. The chemical substance loses its colour when any of these properties are not satisfactorily present in them. Dyes also contain another substances called auxochromes which are called colour helpers. Carboxylic acid, sulfonic acid, amino, and hydroxyl groups are few of the auxochromes. These auxochromes are not reasonable for the colour of the colourant but are used to change the dye solubility. Pigments are also coloured substances but they are different from dyes in the way that they normally are insoluble and has no tendency to attach to. The dyes are classified as naturally occurring or synthetic/artificial. The colourants which are obtained from plants, minerals or any naturally occurring substances are called Natural dyes. Highest percentage of naturally occurring dyes are obtained from plant sources like roots, leaves, bark and wood of trees. Increased demand for readily available, inexpensive, and easily applied dyes led to the invention and rapid growth of synthetic dyes.

The presence of dye or colour and its conducive compounds have forever been unwanted in water for the use in either industrial or domestic requirements. Colour may be a visible waste product. Various types of coloring materials like dyes, tanning, inorganic pigments, lignin etc. all impart colour. Amongst complicated industrialized effluent with numerous sorts of coloring materials, dye wastes are major. At present there are more than 8 thousand various kinds of dyes in market having different chemical properties. The pharmaceutical industries, dye and dye intermediates industries [1], Kraft bleaching [2], paper and pulp industries [3] are different

industries using dyes. Other industries include tannery [4], fabric industries [5], cosmetics, paper, rubber etc. Colour of a dye is mainly because of dye intermediates and organic colorants [7]. Colour removal from industrial effluents is one amongst the foremost and the toughest demand faced by the paper and pulp industries, textile finishing, dye producing, attributable to noxious nature of dyes. Based on ions present in it, dyes are mainly classified in three categories: (a) direct, acid and reactive dyes (anionic), (b) all basic dyes (cationic) and (c) dispersed dyes (nonionic).

1.3 Harmful Effects of Dyes

All the dye wastes, which are produced from various types of industries, might have harmful impacts on microbial inhabitants and may be unhealthful and even fatal to mammals. These dyes may source for allergic eczema, skin irritation problem, mutations and cancer. The few chemicals used to produce dye are highly toxic, carcinogens and hormonal disrupter. The excessive use of dyes causes ecosystem problems in the environment. This not solely avoids sunrays penetration into water and decreases photosynthetic activity but also results in causing difficulties within the atmosphere.

Malachite green is unsafe dyes which not only possess extremely toxic properties affecting the cells of mammals but also is a major cause of creating tumor in liver. The dye discharged in water bodies without being treated properly, hampers the life-cycle of aquatic animals and plants by obstructing the penetration of sunlight [8]. They cause lack of dissolved oxygen due to conjointly increase in the biological oxygen demand (BOD) to sustain aquatic life. Since some dyes are terribly cyanogenics, they cause direct damage or inhibition of their chemical action abilities. At low concentrations, dyes have an effect on the marine life and therefore, the food cycle. As per its design, dyes are very stable molecules, created to fight against the degradation by light, biological, chemical and other areas [9].

These days approximately a million metric tons of dyes are produced annually in the world of azo dyes ($R_1-N=N-R_2$), which signify about 72% of the total dyes [10]. About 60,000 metric tons of dyes are being produced in India, which is very close to 6.6% of total world production [11]. According to the recent survey, about two third of its market are being used in textile industries. It has been indicated that 14% of the artificial textile dyes used every year are thrown to water streams. Waste water treatment plants are the major sources of these to the

environment [12]. Due to the contumacious nature and complexity in structure of dyes, it is very difficult to decolorize dyes, which make it compulsory to get rid of them from industrial sewages before being thrown out into main stream [13]. The effluent from a dye house usually contains 0.5–0.7 g dye l⁻¹ [14].

1.4 Removal Methods

Thus, the removal of this colour is one of the intimidating tasks for the fisheries industries, textile finishing, dye producing, Kraft bleaching and tannery industries and pulp and paper among others. Chemical oxidation, membrane separation etc. are the various ways used to remove dyes from waste water. Other processes include aerobic/anaerobic processes, electrochemical method, agglomeration etc. Because of being expensive and inefficient, most of these processes are not used on large scale [15]. Coagulations and chemical and electrochemical oxidations have low practicability on large scale plants [15]. Adsorption is preferable over these processes and is widely used because of low cost and high performance [15]. Activated carbon is the most common adsorbent used. Metal hydroxides, alumina, silica etc. are other common ones. Economic benefits, performance efficiencies and environment are primary considerations while choosing an adsorbent, therefore researchers usually cheap and best adsorbents, which are usually waste materials such as char [15].

Activated carbon is being used as an absorbent in most of industrial systems use for removal of dyes in wastewater attributable to its notable adsorption capability. [16-18]. However because of high price of activated carbon, adsorption is preferred by using cheaper materials. Various literature studies have shown that many lesser price materials are been successfully used for the exclusion of dyes from aqueous solutions. However, very few of those can be used well to separate dye from the waste stream. Therefore, through this project the potential of yet one more new waste matter (orange peel) which is accessible in abundance in India has been explored.

1.5 Objective of the present work

The purpose of this project work is

- To investigate the feasibility of orange peel for the removal of malachite green dye from aqueous solutions

- To determine the various physiochemical controlling factors affecting adsorption including pH, adsorbent concentration, initial concentration of dye, time of contact and temperature.
- To characterize the adsorbent by proximate analysis, particle size, SEM, FTIR values and BET surface areas .
- To state kinetic and thermodynamic parameters for explaining the nature of adsorption process, and
- To define the practicability of various Isotherm models for the best-fit Isotherm equation.

Chapter 2

Literature Review

2. LITERATURE REVIEW

2.1 Synthetic Dyes

The dyes which are not naturally occurring and are produced by human beings are called synthetic dyes. They impart better properties to the materials they are applied upon and are also less expensive and also have vast options to be chosen from. Due to these properties, they have replaced the natural dye in a very short span of time. Today, the scenario is such that we can see synthetic dyes almost everywhere, ranging from paper, food, clothes and many more. They are also used in rubber industries, cosmetics etc. But even though with so many advantages, synthetic dyes are very harmful for the mankind as well for the environment. That is why there are number of methods being applied these to separate these dyes from water. However, most the processes used are costly and not very effective. The benefits and limitations of different treatment methodologies besides rising technologies are given in Table 1(a) and 1(b).

2.2 Adsorption

Adsorption is the process in which different molecules, ions and atoms of a liquid or gas get attached to the surface [19]. Adsorbate is attached in the form of a film on the surface of the adsorbent. This process is different from absorption since in absorption, the substrate which is usually in the form of fluid percolates into the absorbent [20]. Thus absorption includes the whole matter whereas adsorption is only effective on surfaces. But both the terms are included in a single term called “sorption”, and the reverse of “sorption” is called “desorption”. Adsorption is proving to be a better and more efficient method of waste water treatment in recent years. It is the process of formation of a layer of solid or gas on the substrate. Thus in the process of adsorption, the substance gets separated from fluid phase and gets accumulated on the solid phase substrate [21].

2.3 Mechanism of adsorption

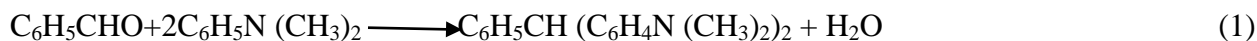
Adsorption process involves three steps. First of all, the substance which has to be adsorbed i.e. adsorbate enters to the outer surface of substance which adsorbs it i.e. adsorbent [22]. After that, the adsorbate move into the openings/pores of the adsorbent particles. Higher the surface area of the pores, higher will be the adsorption. And finally the molecules get attached to the surface area of adsorbents. [22]. Thus adsorption is a surface phenomenon. It occurs because of the interparticle forces of attraction between molecules or ions of adsorbate and adsorbent [22].

2.4 Adsorbate

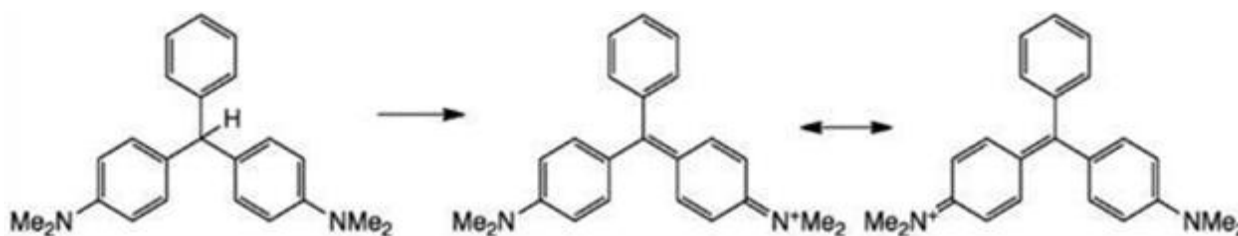
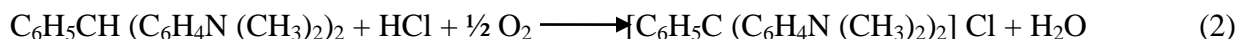
The adsorbate used, Malachite green is an organic compound that is used in various industries as dyestuff. It has been used as a colouring material for paper, leather and silk since long. The compound has no relation with the mineral malachite. It is called malachite green just because of the similarity of colour between them.

In industries using dyestuffs, as well as pigments, it is used a triarylmethane dye. In actual form, Malachite green refers to the chloride salt $[C_6H_5C(C_6H_4N(CH_3)_2)_2] Cl$, but the term Malachite green just refers to the coloured cation. It is also available in the form the oxalate salt which is used in this project. The colour of the compound is not affected by the oxalate and the anions. In fact the acute green color of the cation is only because of its absorption band which lies in the green region. Malachite green dye is basically a cationic dye.

The preparation of malachite green is a two-step process. In the first step, leuco malachite green LMG is prepared by the condensation of Benzaldehyde and dimethyl amine [1, 2]:



In the second step, malachite green compound is obtained by the oxidation of this colorless leuco compound into the cation.



The equilibrium isotherm analysis and the kinetic study for the removal of malachite green dye from aqueous solutions by adsorption using pulp fly ash and activated carbon has been studied. Adsorption studies were conducted in batch form to examine the impact of different parameters on dye removal. The parameters included like contact time, adsorbent dosage, pH, and the initial concentration of malachite green. The strong effect of solution's initial pH was found on the chemistry of each-the dye molecules as well as the adsorbents in the solution. The equilibrium contact time came out to be 4 hour. The optimum

doses of BFA, ACC and ACL were also calculated. The second order kinetics has being followed [23].

The use of deoiled soya which is an agricultural waste has been also used for the malachite green removal and recovery. Batch adsorption techniques were used for primary study including concentration of deoiled soya, contact time, sieve size etc. IR and DTA curves were used for the characterization of the adsorbent. Freundlich and Langmuir models suggested the sustainable mechanism of the involved process involved. The rate constant is relevant to first order rate expression which was determined after finding out specific rate constant Thermodynamical parameters have also been calculated [23]

In the study based on “Removal of dyes from aqueous solutions by cellulosic waste orange peel”, the study has been conducted on three different dyes- Rhodamine-B, Procion orange and Congo red, by waste orange peel. The initial pH of the solution, adsorbent dosage etc. were examined. Two isotherm models- Freundlich and Langmuir were being obeyed by the adsorption process. The uptake capacity was found to follow “first-order” rate kinetics. Low pH was favorable for all the three dyes’ adsorption. In contrast, the study of desorption experiment showed alkaline pH to be efficient for desorption [26]. The adsorption of malachite green dye using bentonite as adsorbent in a batch absorber has also been studied and the various effects of parameters of adsorption onto bentonite has been found out. The removal of dye was found to enhance with increasing contact time till equilibrium was reached and initial dye concentration and also the sorption capacity of adsorbent used is not affected by the initial pH range of 3-11 [27].

The “Removal of malachite green from aqueous solutions by adsorption on oil palm trunk fiber” was carried out where the variables which were operating were concentration of dye initially, contact time for adsorption and pH. The multilayer adsorption isotherm, the Langmuir and the Freundlich isotherm analyzed the data of equilibrium adsorption. With increasing concentration of malachite green dye, the pore-diffusion coefficient was enhanced whereas the film-diffusion constant was diminished [29].

Yet another “Biosorbent- neem sawdust” has also been used as an adsorbent for the “removal of malachite green dye from an aqueous solution”. Varied conditions of experiment like time needed for efficient agitation, concentration of dye, adsorbent dosage, pH of the solution to estimate “the potential of neem sawdust for the removal of malachite green dye from wastewater”. As the initial concentration of dye is decreased and the adsorbent dosage increased, the percent removal of dye also increases [32].

Table 1(a): Available Methods for treatment of dyes

Treatment Methodology	Stage of treatment	Type of Industry	Advantages	Limitations
<i>I. Physical Methods</i>				
1.Adsorption a. Activated Carbon b. Bagasse c. Peat d. Wood chips	Pre/post treatment Pre treatment Pre treatment Pre treatment	Brewery/tannery/textile Sugar/Brewery Any industry Any industry	Economical, good removal efficiency Waste recycling No activation required Good adsorption for colourants	Regeneration is costly Post treatment disposal Lower surface area Huge quantity required
2.Irradiation	Post treatment	Kraft mill, paper and pulp	Effective removal at low volumes	Requirement of dissolved Oxygen
3.Ion Exchange	Main treatment	Any industry	Low cost regeneration	Limited applications
<i>II. Chemical Methods</i>				
1.Oxidation a. Fenton's Regeneration b. Ozonation c. Electrochemical oxidation	Pre treatment Main treatment Post treatment	Textile Brewery/Distillery Kraftmill	Wide range of decolourization Effective for both soluble and insoluble dyes	Expensive Unsuitable for dispersed dyes Cost intensive
2.Coagulation	Pre treatment	Sugar/Pulp and paper	Low capital costs	Dewatering and sludge handling problems
<i>III. Biological Methods</i>				
1.Aerobic Process	Main treatment	Kraftmill/Tannery	Colour as well as COD removal	Longer detention time needed.
2.Anaerobic Process	Main treatment	Pulp and paper/sugar/distillery	Biogas produced for steam generation	Longer acclimatization phase
3.Single Cell(Fungal, Algae/Bacterial)	Post treatment	Any industry	Good removal efficiency for low concentrations and volumes	Cost intensive, unable to treat large volumes

Table1 (b): Emerging technologies for treatment of dye

Treatment Methodology	Stage of treatment	Type of Industry	Advantages	Limitations
1.Advanced Oxidation Process	Main treatment	Distillery/Textile	Insurance of mineralization, enhances biodegradability	Expensive process
2.Membrane Filtration	Main treatment	Brewery/Tannery	Wider application for complex wastes	Dissolved solids are not separated
3. Photocatalysis	Post treatment	Any industry	Shorter detention times, atoxic and inexpensive	Effective only for small amount of colourants
4.Engineered Wetland Systems	Pre/post treatment	Any industry which release large volumes of effluents	Can be operated on large volumes of water cost effectively	Difficult to manage during rainy season, high installation cost
5.Enzymatic Treatment	Post treatment	Any industry after biological treatment	Unaffected by shock loadings, effective for specifically selected compounds	Tedious work of isolation and purification of enzyme, presence of interferences
6.Sonication	Pre treatment	Any industry	Simple in use, very effective in integrated systems	Relatively new method, full scale application is still awaited
7.Redox Mediators	Pre/supportive treatment	Any industry after biological treatment	Easily available, enhances the process by increasing the electron transfer efficiency	Dependent on biological activity of the system

Chapter 3

Materials and Methods

3.1 MATERIALS

3.1.1 Instruments

Table 2 gives the list of instruments used in this project work, their manufacturers, functions and the operating conditions

Table 2: List of Instruments

Instrument	Manufacture	Function	Operation conditions
<i>Analytical balance</i>	Sartorius (BS223S)	Weight measurement	1mg - 100g
<i>pH meter</i>	Systronics (361)	Measurement of pH	pH 1 to 12
<i>Incubator shaker</i>	Environmental orbital Shaker	Shaking of conical flasks containing samples	<ul style="list-style-type: none"> • Speed: 120 rpm. • Temperature: 25°C-40°C.
<i>Scanning Electron Microscope</i>	JEOL (JSM-6480 LV)	To study the clear morphology about the structure and extent of Orange peel samples.	<ul style="list-style-type: none"> • Magnification: up to 10000X • Resolution : 1µm • Detector: Everhardt Thornley secondary electron detector and Solid state Backscattered detector.
<i>Micro Centrifuge</i>	Remi (RM12C)	Separation of undissolved dyes from the solutions	<ul style="list-style-type: none"> • 8000 RPM for 10 min
<i>UV-vis Spectrophotometer</i>	Labindia	To determine the absorbance	<ul style="list-style-type: none"> • Wavelength-582nm
<i>Brunauer–Emmett–Teller (BET) Surface Area Analyzer</i>	Quantachrome Instruments	To determine the surface area and pore size of the sample.	<ul style="list-style-type: none"> • Degassing of N₂ gas at 70°C
<i>Fourier Transform Infrared Spectroscopy (FTIR)</i>	Perkin-Elmer	To predict the organic compounds present in the samples	<ul style="list-style-type: none"> • Resolution of 400 cm⁻¹ • Range 400-4000 cm⁻¹ • Temp-500 °C
<i>Hot Air Oven</i>	WEIBER	For drying of samples	<ul style="list-style-type: none"> • Done at 70°C for 8 hours maximum
<i>Oven and Furnace</i>	WEIBER, ADCO Electric furnace	For proximate analysis: ASTM-D-3172,3173,3174,3175	<ul style="list-style-type: none"> • As per standards

3.1.2 Chemicals and Glasswares

All reagents used during the project were of analytical grade and all solutions were prepared using distilled-water. Glasswares used for the experiments volumetric flasks, pipette, weighing cylinder etc. are all made up of Borosil and are obtained from Tarson Product Private Limited. All the glasswares were rinsed thoroughly with water several times (tap water) and followed with distilled water and finally were dried in hot air oven to remove any trace of moisture present.

3.2 METHODS

3.2.1 Preparation of Adsorbent

Oranges are found in abundance in India. Their peels can easily be obtained from any juice shop. Since peels does not have any significant use, they are treated as waste materials and thus are available in plenty at free of cost. First of all the orange peels were thoroughly washed to remove dirt and unwanted particles adhered to it. They were cut it small pieces for making it easy to grind them. The small pieces of peels were kept in hot air oven at a temperature of 70°C for 8 hours .After drying, the pieces were crushed in a mixer grinder until they became fine powder. The powder was sieved so that all the particles to be used are of similar size. Finally the orange peel powder was stockpiled in air tight packets so that they can be used in future without any further treatment.

3.2.2 Adsorbate

Malachite green dye is the adsorbate, its colour is green. It gives green colored solution in aqueous phase. It is a basic cationic dye and has chemical formula as $C_{25}H_{34}N_4O_2$. The molecular weight of malachite green dye is 326, $\lambda_{\text{max}} = 618 \text{ nm}$ [1].The aqueous solutions of varied concentrations of malachite green dye was prepared by dilution from its stock solution and the study were done by varying different parameters.

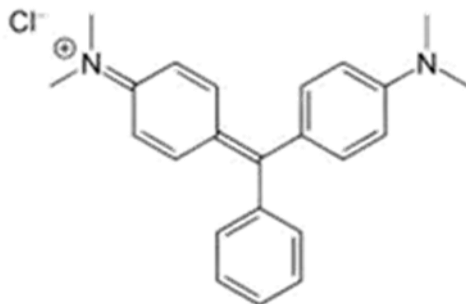


Fig 1. Structure of Malachite Green

3.2.3 Experimental Procedure

The adsorption of malachite green dye using orange peel powder was studied using the batch techniques. First of all, the stock solution of 1000 mg/L of dye was prepared by dissolving 1000mg of malachite green dye in 1000 ml ethanol. Ethanol has been used to dissolve malachite green particles effectively in the solution. First of all, two dye solutions of concentration 20 ppm each were prepared from the stock solution and 1gram of adsorbent i.e. orange peel powder was added to one of them. The solution with adsorbent was kept in a shaker for 120 minutes at 120rpm under normal conditions. After 2 hours, it was taken out and allowed to centrifuge at 8000rpm for 10minutes to separate all the undissolved particles. Then both the solutions-the solution with adsorbent and the one without the adsorbent were analyzed in a UV-vis spectrophotometer. The results obtained from the spectroscopy confirmed that the considerable amount of dye was adsorbed on adding orange peel powder. Thus the further studies were feasible.

Here it is important to mention that we tried to study the scope of sweet lime too for the removal of malachite green dye from water. Sweet lime in the powdered form was mixed in one of the solutions just as the orange peel samples as mentioned above. But the results were not satisfying and we came to conclusion that sweet lime cannot be used as adsorbent for the removal of malachite green and thus we further focused our study only on orange peel adsorbent. Another notable thing is that when we tried to separate the undissolved particles of dye from the solution by filter paper, then the paper also adsorbed some of the dye during the process. This affected the final readings in the spectroscopy. Thus for our whole project, we used centrifuge instead of using filter paper. Furthermore, first of all we prepared five workings solutions of varying concentrations from 20-400ppm. The same procedure was applied and the results were

plotted to get the calibration curve. This curve served the basis for all future calculations during the complete project work.

3.2.3.1 Study of contact time

A dye solution of 20mg/l was prepared by diluting the stock solution. This solution was maintained at pH 4.5 and 1gram of orange peel adsorbent was added to it. Then the solution was kept in shaker for 180 minutes at room temperature. The solutions were taken out at different intervals of time. And finally, all the samples of different time intervals were analyzed and compared with the initial sample which was without adsorbent to find out the percent removal of dye and the effect of contact time on it.

3.2.3.2 Study of pH

Five working solutions of concentration 20mg/l each were prepared. They were maintained at different pH ranging from 2-10 by adding 0.1N HCl or NaOH. Again 1 gram adsorbent was added to each of them and kept in shaker at room temperature and at 120 rpm for 2hours. The solutions were taken out after two hours and centrifuged and analyzed in UV-spectrophotometer to compare the effect.

3.2.3.3 Study of adsorbent Dosage

Standard dye solutions of 20mg/l were prepared once again from the stock solution. To each of these solutions, adsorbent was added but in varied amount of 0.5gm, 1gm and 1.5gm respectively. These three solutions containing different amount of adsorbent dose were then again put into the same procedure of shaking, centrifuging and spectrophotometer analysis. And the results were used to study the effect of adsorbent dosage on the dye removal.

3.2.3.4 Study of Initial dye concentration

Standard dye solutions with different concentrations ranging between 20-200 mg/L were prepared by dilutions to be used as working solutions. To all these solutions, 1gram of orange peel powder was added as adsorbent. The pH of the solutions was maintained at 4.5.

3.2.3.5 Study of temperature

100ml solutions of concentration 20mg/l were prepared from the stock solution by diluting. To all these three solutions, 1gm of adsorbent was added and they were maintained at pH 4.5. The solutions were kept for shaking at 120 rpm for 2 hours but at different temperatures of 20°C, 30°C and 40°C. After completion of 2 hours, they were taken out of the shaker, put to centrifuge at 8000rpm for 10 minutes and then analyzed in UV-spectrophotometer.

In all these study of different parameters, the amount adsorbed is calculated as:

$$q_e = \frac{C_0 - C_e}{X} \quad (3)$$

Where, q_e = Amount of dye adsorbed per unit mass of adsorbent (mg/g).

C_0 = Initial dye concentration (mg/L).

C_e = Final dye concentration (mg/L).

X = Dose of adsorbent (g/L).

Also the removal efficiency of sample is calculated as:

$$\% \text{ Removal} = \frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} * 100 \quad (4)$$

3.2.4 Adsorption Isotherms

Adsorption is typically represented through isotherms, that is, the quantity of adsorbate on the adsorbent as a function of its pressure (in case of gas) or concentration (in case of liquid) at a constant temperature. Amount of adsorbate adsorbed is almost continuously normalized by the mass of the adsorbent to permit comparison of various materials. Equilibrium studies on adsorption process provide data on the capacity of the adsorbent. Also, an adsorption isotherm is characterized by particular constant values that exhibit the surface properties and affinity of the adsorbent and can even be used to compare the adsorptive capacities of the adsorbent for various pollutants. The most common model at constant temperature for this sort of adsorption Langmuir or Freundlich model.

3.2.4.1 Langmuir Isotherm

Assumptions of Langmuir Isotherm are:

- 1) The surface available of the adsorbent for adsorption is assumed to be uniform, that is, all the sites available for adsorption are equivalent.
- 2) There is no interaction between molecules of adsorbed materials.
- 3) There is same mechanism for all sort of adsorption.
- 4) Only a monolayer is assumed to be formed at the site of maximum adsorption, i.e. molecules of adsorbate do not deposit on another molecules of adsorbate which are already adsorbed. Instead, they only deposit on the remaining surface available for the adsorption

$$\frac{C_e}{q_e} = \frac{1}{q_m} \cdot \frac{1}{K_L} + \frac{C_e}{q_m} \quad (5)$$

C_e-concentration at equilibrium

q_e- amount of adsorbate adsorbed per gram of adsorbent at equilibrium;

q_m- Langmuir constants related to adsorption capacity

K_L- Langmuir constants associated with energy of adsorption,

The Langmuir constants q_m and K_L are calculated from the slope and intercept of plot between C_e/q_e vs C_e.

3.2.4.2 Freundlich Isotherm

Freundlich isotherm theory describes the quantitative relation i.e. the ratio of the quantity of adsorbate adsorbed onto a given mass of adsorbent to the concentration of the adsorbate in the solution. It is applicable to adsorption on heterogeneous surfaces and can be represented by equation in linear form as:

$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n_f} \text{Log } C_e \quad (6)$$

The plot of Log q_e versus Log C_e provides the slope 1/n_f and intercept K_f ((mg/g)/ (L/g)ⁿ) K_f is

the Freundlich constant and n_f is the Freundlich exponent. Here, K_f and n_f are defined as the constants for the adsorption capacity and intensity of adsorption respectively.

3.2.5 Kinetic Studies

The adsorption on orange peel sample can be analyzed by kinetic model which used to determine the potential adsorption mechanisms. In the present study, pseudo-first order kinetic model and pseudo-second order kinetic model have been suggested to explain the process of adsorption which depends on the adsorbent characteristics.

A pseudo-first order kinetic model suggested by Lagergren is as follow in its integrated form:
:

$$\log (q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303}t$$

(7)

Here q -quantity of dye adsorbed at particular time t (minute),

q_e - quantity of dye adsorbed at equilibrium

k_1 - rate constant of pseudo-first order adsorption.

The kinetics of adsorption can also be analyzed by a pseudo-second order reaction. Following gives the integrated linearized form of the model:

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t$$

(8)

Where k_2 in the above equation is the pseudo-second order rate constant for dye adsorption on the sample. The plot of t/q versus t for the above equation 8 will give a linear relationship, from which q_{eq} and k_2 can be calculated from the slope and intercept of the plot, if second order kinetic equation is valid.

3.2.6 Thermodynamic Study

The parameters for thermodynamic study, particularly Gibb's free energy, enthalpy and entropy have a significant role to know the spontaneous and heat change involved in the adsorption process. Equilibrium constant can be used to calculate the thermodynamic parameters mentioned above. A standard equation called the van't Hoff equation is employed to determine equilibrium constant with change in temperature which is given as follows:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

(9)

Integrated form of equation (9) can be represented as follows:

$$-\ln K = \frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + C$$

(10)

If C is written as: $C = (\Delta S/R)$ then, $\ln K$ can be obtained as below:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R} \left(\frac{1}{T} \right)$$

(11)

The slope and intercept of line obtained by plotting $\ln K$ versus $1/T$ gives enthalpy and entropy changes of the process.

Eq. (11) can be combined with the equation $\Delta G = -RT \ln K$ to obtain the free energy change in terms of change in enthalpy and change in entropy as follows:

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

3.2.7 Desorption Studies

The study of desorption process helps to understand the mechanism of adsorption and also the scope of recovery of adsorbate as well as adsorbent. If the adsorbent is can be successfully regenerated, then it will make the treatment process more economically advantageous. A dye solution of 20mg/L was prepared in two different flasks with adsorbent dose of 1gL^{-1} . The prepared solutions were kept in the shaker for the required time and the final readings were noted down after the attainment of equilibrium. The separation of adsorbent was done by centrifugation and the obtained sample is dried for 10-12hrs. After the drying of

adsorbent having adsorbed dye sufficiently, they were put in distilled water at different pH. The final readings of concentration were noted down.

3.3 Characterization of sample

3.3.1 Proximate Analysis

3.3.1.1 Moisture Content

A crucible with lid was taken and weighed. 1gram of sample was taken in the crucible with lid and weighed. It was kept in hot air oven at 105°C for one and half hours. It was taken out and kept in the desiccator. Then the weight was measured.

$$M = 100 \times \frac{(B-F)}{(B-G)}$$

(13)

Where,

M-moisture content

G- Mass of crucible with lid

B- Mass of crucible with lid plus sample

F- Mass of crucible with lid plus dried sample

3.3.1.2 Ash content

A crucible was taken and weighed. 1gm of sample was taken in crucible and weighed. The sample was kept in a muffle furnace for one and half hours at a temperature of 6500C. Then it was taken out and kept in a desiccator for half an hour to cool down. Then again the weight is measured.

$$A = 100 * \frac{(F-G)}{(B-G)} \quad (14)$$

Where,

G- Mass of empty crucible

B-mass of crucible plus sample

F-mass of crucible plus ash sample

3.3.1.3 Volatile Matter

A crucible with lid was taken and weighed. 1 gram of sample was taken in the crucible with lid and weighed. It was kept in the muffle furnace at a temperature of 910°C for 7 minutes. Then it was taken out and kept in the desiccator for half an hour to cool down. The weight of the sample in crucible with lid was taken.

% Volatile matter was then calculated as,

$$V = 100 * \frac{100(B-F) - M*(B-G)}{(B-G)*(100-M)} \quad (15)$$

3.3.1.4 Carbon Content

Carbon content is calculated as following:

$$\% \text{Carbon} = 100 - (\% \text{ moisture content} + \% \text{ volatile content} + \% \text{ ash content}) \quad (16)$$

3.3.2 BET Analysis

Brunauer-Emmett-Teller (BET) Surface Area Analysis helps in evaluating the specific surface area of sample precisely. In this, the by multilayer adsorption of nitrogen is measured as a function of relative pressure. A fully equipped and automatic operated analyzer is available for this. It gives the idea of physical adsorption of gas molecule on the solid surface using absorption of N₂ gas on the solid material. This is based on the Langmuir adsorption theory of monolayer adsorption to multilayer adsorption based on the following three postulates:

- The physical adsorption of the gas molecule on the solid layer not definite.
- The adsorbed layers do not interact with each other.
- Applicability of Langmuir adsorption theory on each layer.

In this work, BET analysis of the sample i.e the orange peel gave its surface area and pore size and volume values.

3.3.3 FTIR Analysis

Fourier Transmission Infrared Spectroscopy i.e. FTIR technique has been widely used for the prediction of organic compounds present in the sample by the absorption of low energy light i.e. ultraviolet light of each wavelength. We obtain absorption spectra of the compounds which is a unique reflection of the molecular arrangement of the compound in the sample. This spectrum is a graph which contains percent transmittance along Y axis and frequency or wavelength along X axis. By studying the peak between a particular frequencies i.e. gap or band, type of the functional group present can be predicted with the help of available table. For the case of Orange peel, FTIR shows the change in properties of the surface of adsorbent on addition of malachite green dye.

3.3.4 Scanning Electron Microscopy

Scanning Electron Microscope is an electron microscope that produces images of the solid surface by scanning it with electron beam. The electron beams strike the atoms of the sample surface which generates various signals. These signals are detected by electron detector. These signals carry details about the composition and surface structure of the sample. Only the samples of suitable size can be used since they have to be placed in a chamber which only fits the specific size samples. Electrical conductivity at the surface is the most important criteria for SEM characterization of samples. The preparation of the sample is done by coating it with gold to avoid ionization of the sample.

Chapter 4

Results and Discussion

4.1 CHARACTERISTICS OF ADSORBENT

4.1.1 Proximate Analysis

Proximate analysis was performed for orange peel sample to know its different characteristics and carbon content. It shows very less moisture content and volatile matter and ash content are also not very large. The carbon content is reasonably good enough to make orange peel as a good low-cost adsorbent.

4.1.1 Moisture Content

From equation 13,

$$M = 100 \times \frac{(B - F)}{(B - G)}$$

We have,

$$G=37.40$$

$$B=39.40$$

$$F=39.34$$

So Moisture content comes out to be 3%.

4.1.2 Ash content

From equation 14

$$A = 100 * \frac{(F-G)}{(B-G)}$$

Here, G=36.80, B=38.80, F=37.30

So, Ash content is calculated to be 24.5 %

4.1.3 Volatile Matter

Equation 15 gives,

$$V = 100 * \frac{100(B - F) - M * (B - G)}{(B - G) * (100 - M)}$$

B=37.87, F=37.47, M=3, G=36.87

So, % Volatile matter was 38.1%

4.1.4 Carbon content

Using equation 16, it comes out to be 34.4%.

Table 3: Proximate analysis results.

CONTENT	PERCENTAGE
Moisture content	3
Volatile matter	38.1
Ash content	24.5
Carbon	34.4

4.1.2 BET Analysis

The following tabulated results have been obtained for the case of Orange peel. Table 8 gives values of some of the physical properties which were determined by BET. The N₂ adsorption gave the surface area value which is close to the values as recorded in literature for orange peels.

Table 4: BET result for Orange peel.

Properties	Magnitude
Surface area (m ² g ⁻¹)	0.7811
Total Pore volume (cm ³ g ⁻¹)	0.000541
Pore diameter (Å)	23.62

4.1.3 FTIR Analysis

Fig.8 (a) gives the spectra of the FTIR of the orange peel sample before adsorption and table 9 gives the prediction of compounds present in the sample before adsorption; which is confirmed by the peaks between following band.

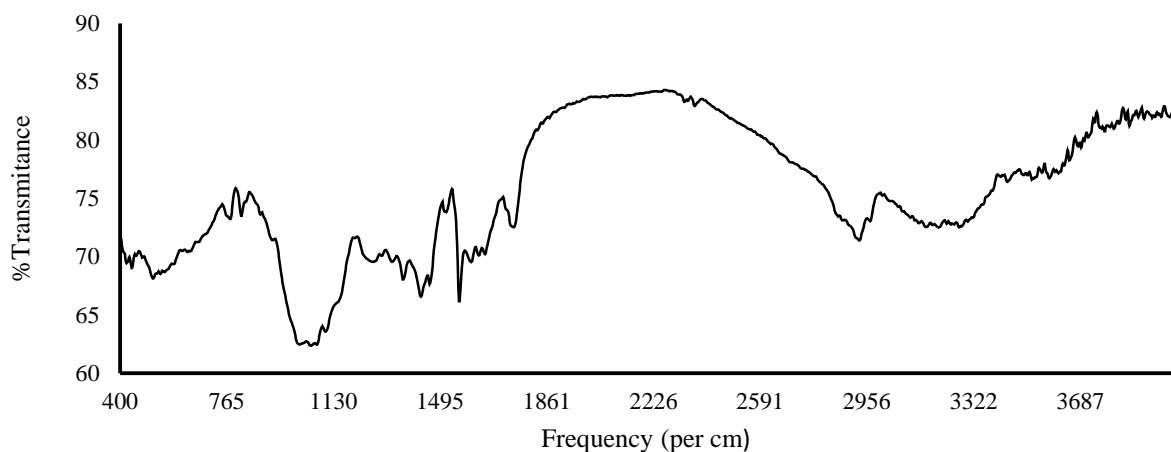


Fig. 2(a): FTIR image of Orange peel before adsorption of malachite green.

Table 5(a): Compounds present in the sample before adsorption of malachite green

Wave number (cm^{-1})	Functional group	Compounds
3300-3200	C-H Stretch	Alkyl
3600-3100	O-H Stretch	Carboxylic Acid
1750-1625	C=O Stretch	Ketone
3100-3000	C=C Bending	Aromatic
1600-1580	C=C Bending	Aromatic
1550-1490&1355-1315	N=O (aromatic)	Nitro group
3400-2400	C=O stretch	Carboxylic acids
1210-1140	P=O	phosphine oxides

Similarly, from the next spectra shown, following functional groups have been found to be present in the Orange peel after adsorption which confirmed by the peaks between following band tabulated below in table 10.

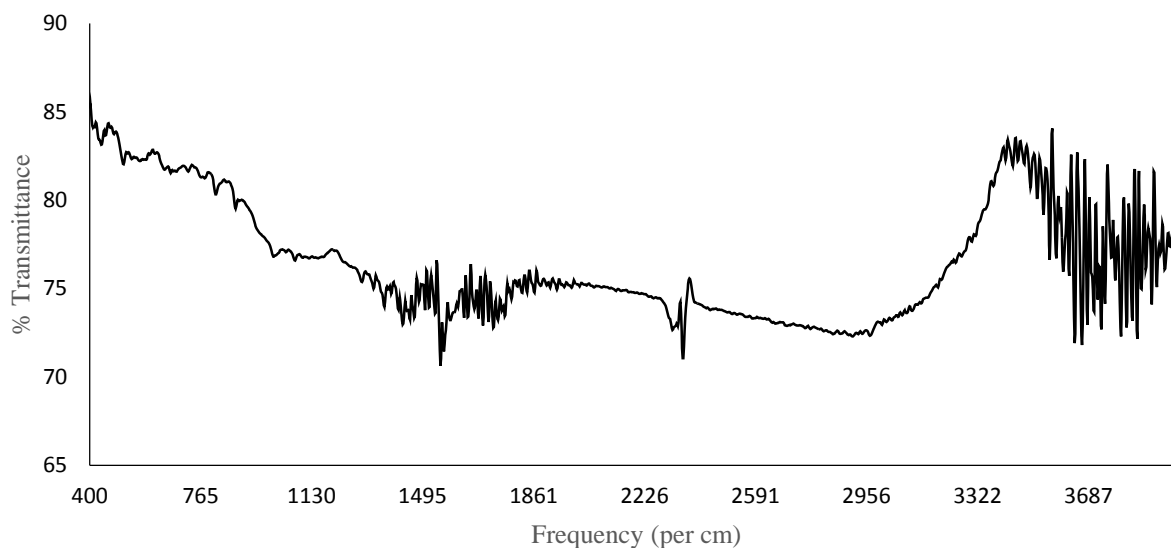


Fig. 2(b): FTIR of Orange peel sample after adsorption of malachite green

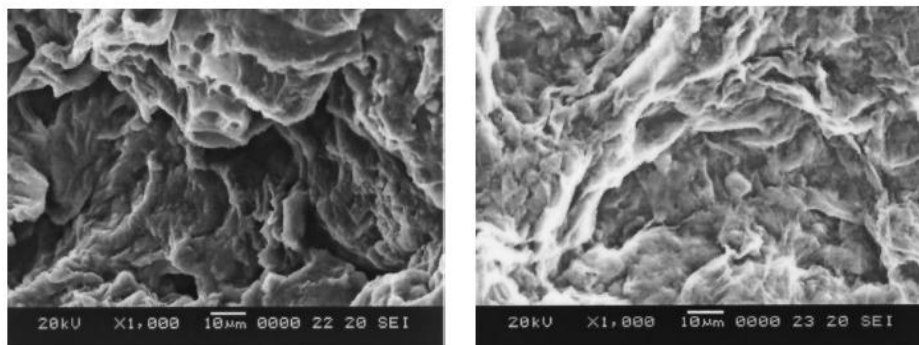
Table 5(b): Compounds present in the sample after adsorption of malachite green.

Wave number (cm ⁻¹)	Functional group	Compounds
3300-3200	C-H Stretch	Alkenyl
2320-2270	P-H stretch	Phosphines
1750-1820	C=O stretch	Anhydrides
3500-3100	N-H stretch	Amides
3400-2400	O-H stretch	carboxylic acids
1600-1500	NO stretch	nitro groups (aliphatic)
1210-1140	P=O	phosphine oxides
690-900	C-H bend (Para)	Aromatics

4.1.4 SEM Analysis

The SEM images of orange peel sample before and after adsorption of malachite green dye have been shown in the figure 9(a) and 9(b) respectively. The orange peels have considerable number of pores for adsorption of dye onto them. Pores within the orange peel particles are heterogeneous before adsorption of dye which is depicted in the image 9(a). After

malachite green dye is adsorbed on orange peel, a significant change is observed in surface topography of the peels. The original orange peels have a highly porous structure whereas peels have a surface partially covered by dye compounds for the used peels.



(a)

(b)

Fig 3 (a) SEM image of orange peel sample before adsorption (b) SEM image of orange peel sample after adsorption

4.2 ADSORPTION STUDIES:

4.2.1 Effect of Contact Time

The impact of contact time on adsorption of malachite green dye can be seen from Fig.2. It is clearly depicted in the figure that the rate of adsorption is very high initially. But at later stages, the rate of adsorption decreases. The concentration of dye does not change significantly after 120 minutes. This gives the equilibrium time for adsorption as 120 minutes. It is primarily because of the saturation of the active sites which do not permit furthermore adsorption to occur.

This can be explained by the fact that initially, the number of surface sites are very large which allows adsorption to take place very easily. But as the time passes, the active sites get saturated thus slowing down the rate of adsorption.

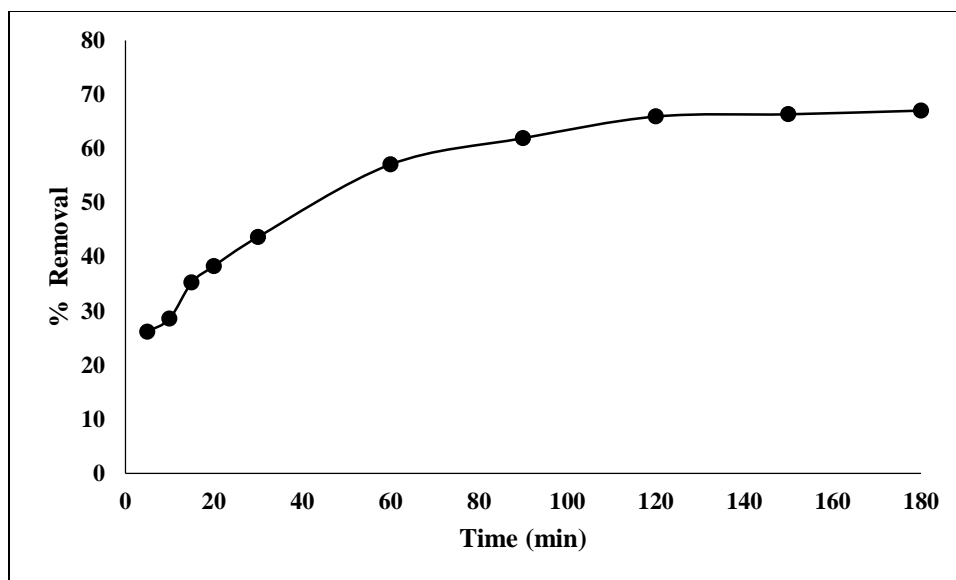


Fig.4.Effect of contact time on the removal of malachite green by Orange peel sample

4.2.2 Effect of Initial pH of the solution:

The initial pH of the dye solution has a very strong impact on the adsorbent's surface properties as well as the degree of ionization of dye molecules. Thus it becomes important to study the effect of pH on adsorption process. Figure 3 shows the effect of initial pH on the amount of dye solution adsorbed by orange peel sample.

In the experiment, 100ml of 200mg/L dye solutions in the pH range 2-10 have been studied. The pH of the solutions were adjusted by using 0.1N hydrochloric acid HCL and 0.1N sodium hydroxide (NaOH) solution using a pH meter. The results are shown in the figure below and it is evident from the graph that the removal efficiency of dye is reasonably high in the pH range 3-5 and declined at higher pH. The higher adsorption at very acidic media could be due to the interactions between the positively charged dyes cations with surface functional groups present in orange peels. On the contrary, at higher pH values, the adsorption decrease which may be because of the formation of soluble hydroxyl complexes.

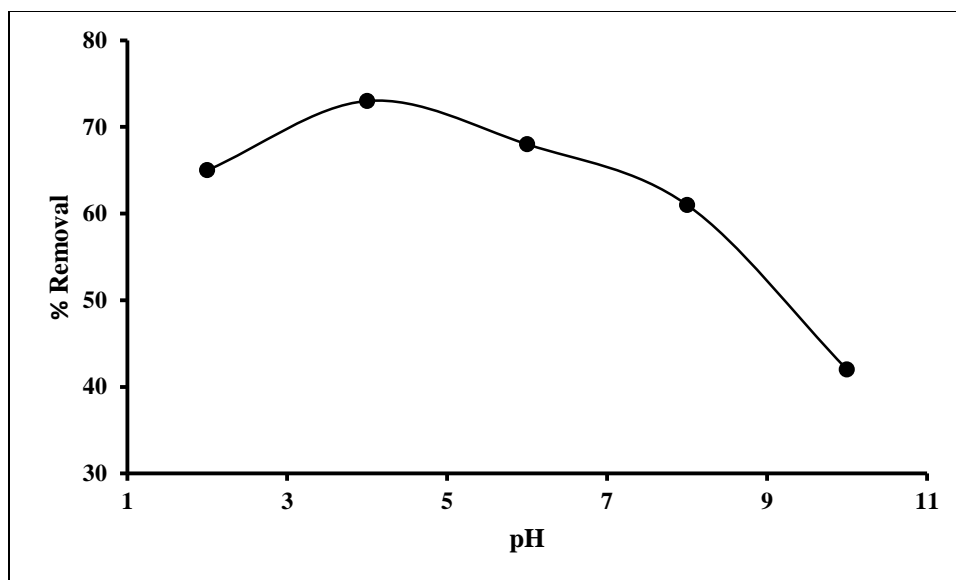


Fig. 5 Effect of initial pH of solution on malachite green removal by orange peel adsorbent

4.2.3 Effect of Adsorbent Dosage

The effects of adsorbent i.e. orange peel sample dosage on the percentage removal of dye at initial concentration of 200mg/l at room temperature was studied for different dosage of 0.5g, 1g and 1.5g in 100ml solution. Figure 4 shows that the percentage removal of dye increases with increase in the adsorbent dosage up to a point but after that there is no significant increase in the removal. This can be explained by the fact that on increasing adsorbent dosage, the surface area of the adsorption sites increases. But there is no significant increase in adsorption capacity further even after adding more adsorbent which might be due to the interactions between particles within themselves.

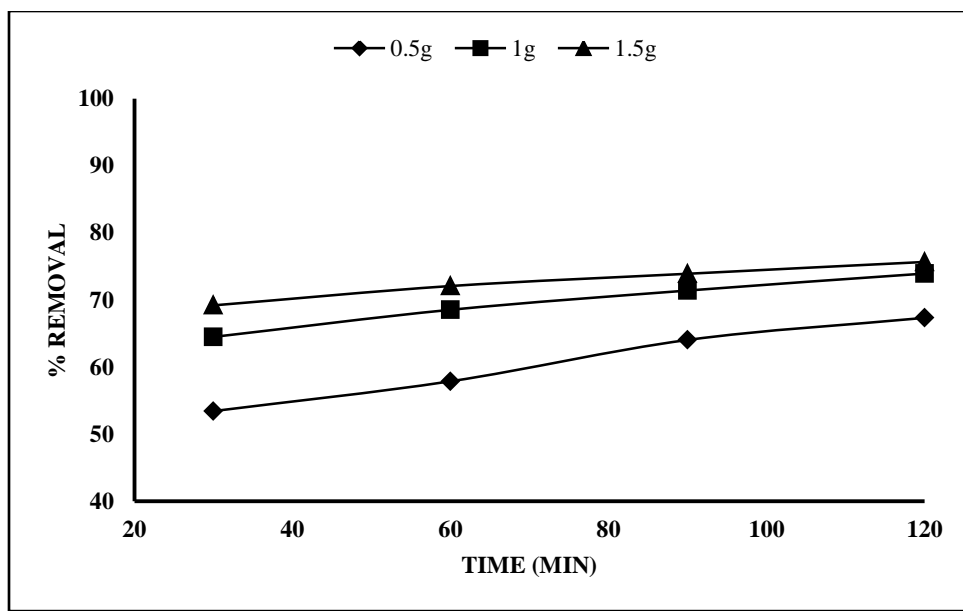


Fig.6 Effect of adsorbent dosage on the dye removal by malachite green solution

4.2.4 Effect of initial dye concentration

The dye concentration has an apparent influence on its removal from aqueous phase. The effect of malachite green dye concentration on the efficiency of adsorption was also investigated in the initial concentration range of 20-400 mgL^{-1} as shown in figure 5. The adsorption capacity of orange peel at equilibrium increases with increase in initial dye concentration. This trend could be attributed to the fact that at high concentration of dye, there is high driving force for mass transfer. In addition, if the dye concentration in the solution is higher, the active sites of adsorbent are surrounded by higher number of dye molecules which leads to more efficient adsorption.

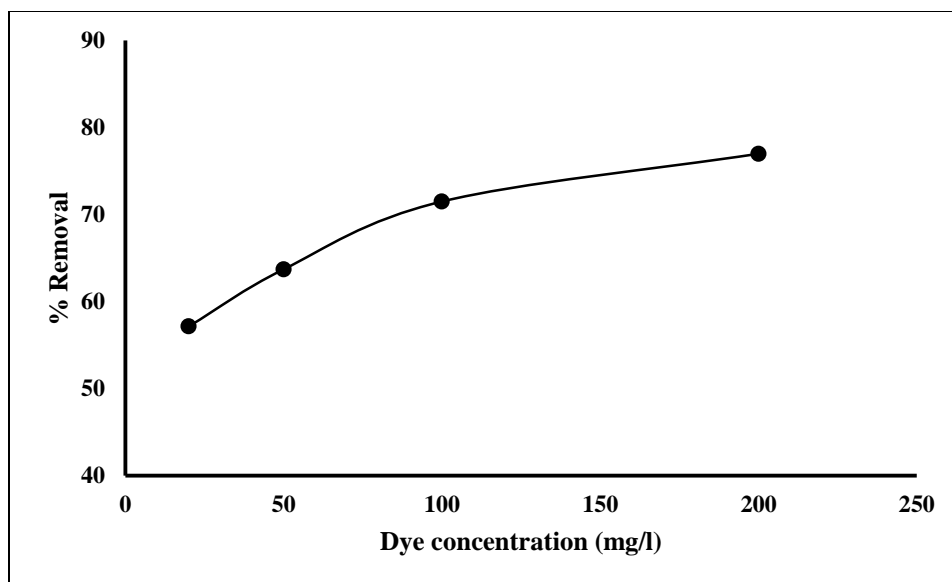


Fig. 7 Effect of initial dye concentration on the removal of malachite green by orange peel adsorbent

4.2.5 Effect of Temperature

Temperature is also a notable controlling factor in the real applications of adsorbent for the dye removal process. Figure 6 represents the adsorption of malachite green by orange peel at different temperatures. The temperature affects the dye adsorption efficiency positively which means that the percentage removal of dye increase on increasing the temperature of the system. This trend can be attributed to the fact that the chemical interactions taking place between malachite green dye and the adsorbent is endothermic in nature. This is also suggested by the calculations of thermodynamic parameters.

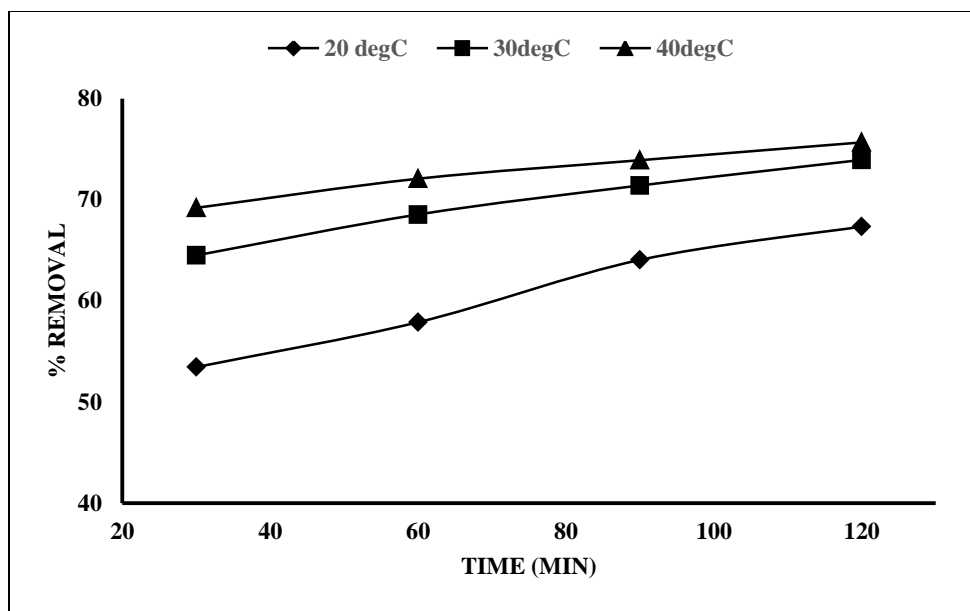


Fig. 8 Effect of temperature on the removal of malachite green dye by orange peel adsorbent

4.3 ADSORPTION ISOTHERMS

The values of the constants of the two isotherms, namely, Freundlich and Langmuir, have been given in the table below. The values for Freundlich and Langmuir isotherm ranges between 0.98-0.99 and 0.86-0.93 respectively for the adsorption of malachite green. It is clearly noticeable that Freundlich model is better fit in the adsorption isotherm model (Table 6). This shows that adsorption of the dye follows heterogeneous coverage which has overlapping layers.

Table 6: Evaluated adsorption constants at different Isotherm models:

Adsorbent dose	Langmuir isotherm			Freundlich isotherm		
	K_L	q_m	R^2	K_f	n	R^2
0.5g	10	25	0.934	0.73206	172.0869	0.984
1g	2.684	19.6078	0.924	1.6638	43.7284	0.994
1.5g	2.446	45.45	0.860	1.2239	52.03934	0.980

4.4 KINETIC STUDIES

The adsorption capacity as well as the percent removal is time-dependent. The process reaches to equilibrium after a definite time. Furthermore, the process at equilibrium depends on initial concentration of dye which is correlated with time. In this work, for all concentrations of dye, the malachite green adsorption reaches equilibrium only at 2 hours or 120 minutes. Also we need to study the kinetics of reaction for which the experimental data were fit into kinetic models. The pseudo-first-order as well as the pseudo-second-order models were analyzed to study malachite green adsorption onto orange peel sample. The best-fit model was determined based on the values of correlation coefficient. Our experimental results tend to follow the pseudo second-order model better (Table 7). It was observed from Table 7 that Malachite green adsorption on orange peel powder followed pseudo 2nd order kinetics. R^2 values are 0.97 and 0.75.

Table 7: Pseudo 1st order and pseudo 2nd order Parameters

Order	Co(mg/l)	Q _{e,exp} (mg/g)	Q _{e,cal} (mg/g)	K ₁ (l/min)	R ²
Pseud1 st order	20	9.8	13.4	0.029	0.973
Pseudo2 nd order	20	9.8	0.25	0.164	0.752

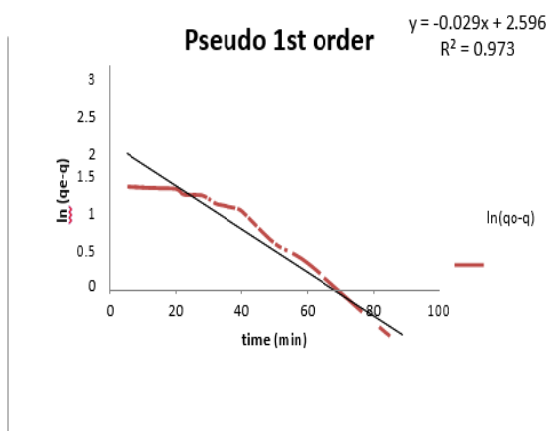


Fig 9(a): Pseudo 1st order curve

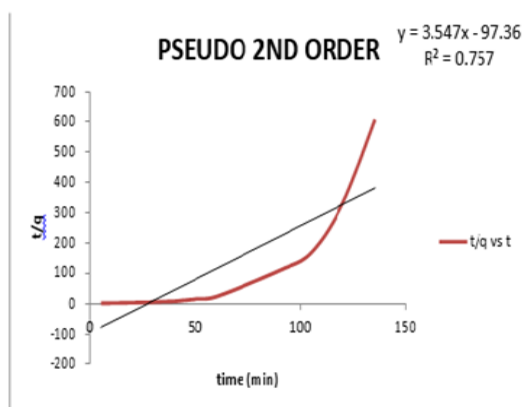


Fig 9(b): Pseudo 2nd order curve

4.5 Thermodynamics Study:

The experimental data calculated were used to carry out the thermodynamic study at different temperatures. ΔG values come out to be negative which suggests that it is a spontaneous reaction (Table 8). Gibb's free energy for the dye has negative values showing the greater adsorption potential. Positive values of ΔH suggest that the process is endothermic in nature.

Table 8: Thermodynamic Constants

MG conc	Temperature(°C)	ΔG (kJ/mol)	ΔS (kJ/mol)	ΔH (kJ/mol)
20	20	-10649.8	85.88	14724.09
	30	-10907.6	85.88	14724.09
	40	-12396	85.88	14724.09
50	20	11239.7	96.35926	17093.58
	30	11932.7	96.35926	17093.58
	40	13180.4	96.35926	17093.58
100	20	-11617	128.9501	26405.26
	30	-12168.2	128.9501	26405.26
	40	-14229.6	128.9501	26405.26
200	20	-11989.9	106.2529	19047.37
	30	-13395.5	106.2529	19047.37
	40	-14100.6	106.2529	19047.37

4.6 DESORPTION STUDY:

The desorption study has been carried out to find out the scope of recovery of dye after the project. The study was conducted at different ranging from low to high. With an increase in pH of the aqueous medium, the amount of desorption is also increased. This is just opposite to the pH effect. It was observed that maximum desorption occurred at higher pH which might be because of the surface sites available. Thus recovery and recycle of adsorbate as well as adsorbent might be possible.

Table 9: Desorption results

pH	Percentage of dye desorbed
2	0.85
10	25.6

Chapter-5

Conclusion

5. CONCLUSIONS

Removal of malachite green dye from aqueous solution using orange peel as adsorbent has been experimentally determined and the following observations are made:

1. Proximate analysis showed good carbon content which favors adsorption. Percentage carbon was found to be 34.4%. The moisture content (3%), volatile content and ash content were also found to be quite reasonable.
2. FTIR spectra show little change in the surface properties of adsorbent after adsorption as compared to that of before adsorption.
3. Scanning Electron micrographs exhibited that orange peel had a considerable number of pores where there is a good possibility of malachite green dye to be trapped and adsorbed into these pores and also there is change in the surface topography of orange peel before and after adsorption of dye.
4. Adsorption tends to increase with contact time. At first the increase in adsorption is very rapid as there are lots of free sites for the adsorption to take place. Rate of adsorption decreases at later stages till saturation is reached due to saturation of active sites. The optimum contact time for equilibrium was found to be two hours.
5. The removal efficiency of adsorbent is maximum in the pH range of 3-5 and declined at higher pH. In the acidic media, the electrostatic interactions between the positively charged adsorbent and negatively charged dye anions whereas at higher pH values the more number of negatively charged anions reduces the dye adsorption due to electrostatic repulsions.
6. As adsorbent dose increases adsorption increases due to the availability of free sites. 1g/100ml concentration of adsorbent is taken as the optimum adsorbate dose. As we increase adsorbate dose more than the optimum the increase in adsorption is very less and it becomes cost ineffective.
7. There is increase in adsorption with the increase in initial dye concentrations due to the high driving force for mass transfer at a high initial dye concentration.
8. Adsorption capacity is found to increase with increase in temperature. At higher temperature mobility of large ions of malachite green dye increases and at high temperature molecules acquire sufficient energy to undergo interaction with the active sites for adsorption.

9. The adsorption process follows pseudo-first-order kinetics and the thermodynamic studies showed that the process is feasible and spontaneous
10. Although the experimental equilibrium data fitted well to Langmuir as well as Freundlich isotherm equations, the Langmuir Isotherm model fitted the best.
11. Desorption studies showed that the recovery and recycling of adsorbent as well as the adsorbate might be possible.

Thus it can be concluded that orange peels, which are waste materials and are in abundance in the country, can be used for the removal of malachite green dye from waste water. Further, there is scope of more study and research which can enhance the percentage removal of malachite green and also, the feasibility of orange peels for removal of other dyes is to be studied.

Chapter-6

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